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ORIGINAL PAPER

A poly(5-indolylboronic acid) based molecular imprint doped with carbon dots for fluorometric determination of glucose

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Abstract A hybrid nanomaterial was synthesized that consists of poly(5-indolylboronic acid) acting as a molecular imprint (MIP), and of fluorescent carbon dots (CDs). The combination of CDs and MIP endowed the hybrid with stable fluorescence and template selectivity. The addition of glucose causes aggregation and quenching of fluorescence. Aggregation is due to the formation of covalent bonds between the cis-diols of glucose molecules and boronic acid side groups. The fluorometric signal, obtained at excitation/emission wavelengths of 350/450 nm, varies in the 5 to 750 μM glucose concentration range, with a 0.5 μM detection limit. The assay is not interfered by various biomolecules including fructose and was successful applied to the determination of glucose in (spiked) serum. In our perception, the results make this glucose assay an attractive new tool for clinical applications.

Keywords Hybrid nanomaterial · Aggregation · Cis-diols · Quenching

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Introduction

Glucose is one of the most immediate energy sources and metabolic intermediates of cells and plays an essential role in cellular metabolism [1]. It has been shown that abnormal glucose transport in the human body may lead to diabetes or some cancers [2]. Regular glucose detection is generally based on electrochemistry [3], colorimetry [4] and spectrophotometry [5, 6]. The electrochemistry approach often suffers from instability, contamination of the electrode, and high cost [7, 8]. Colorimetry- and spectrophotometry- based methods face challenges in continuous monitoring because of interferences from blood colour and slow detection time lags [9, 10]. To solve these issues, it is important to find high-performance glucose detection materials that are simple and low-cost.

Carbon dots (CDs), because of their unique optical properties, have become a rising star in the carbon family and have attracted considerable interest [11, 12]. In addition, most of the CDs reported possess many specialties similar to those of carbon materials and have demonstrated superiority in photoluminescence (PL) performances, such as tunable PL, excellent thermal stability, and high photostability and electrical conductivity, Hence, CDs appear to be promising in the fields of photochemical catalysis, drug and gene delivery, biological detection, and biomedicine [13, 14].

Due to its high stability and selectivity, low cost and ease of preparation, molecular imprinting polymer (MIP) is a promising strategy for biological molecule recognition [15, 16]. It is generally accepted as an effective tool for clinical analysis, environmental monitoring, and diagnostics [17, 18]. Currently, conductive polymers, including polypyrrole, polyindole and polyaniline, have aroused enormous interest for researchers because of their unique electronic, thermal, and optical performances [19, 20]. Moreover, it is generally known that boronic acid groups are the most widely employed

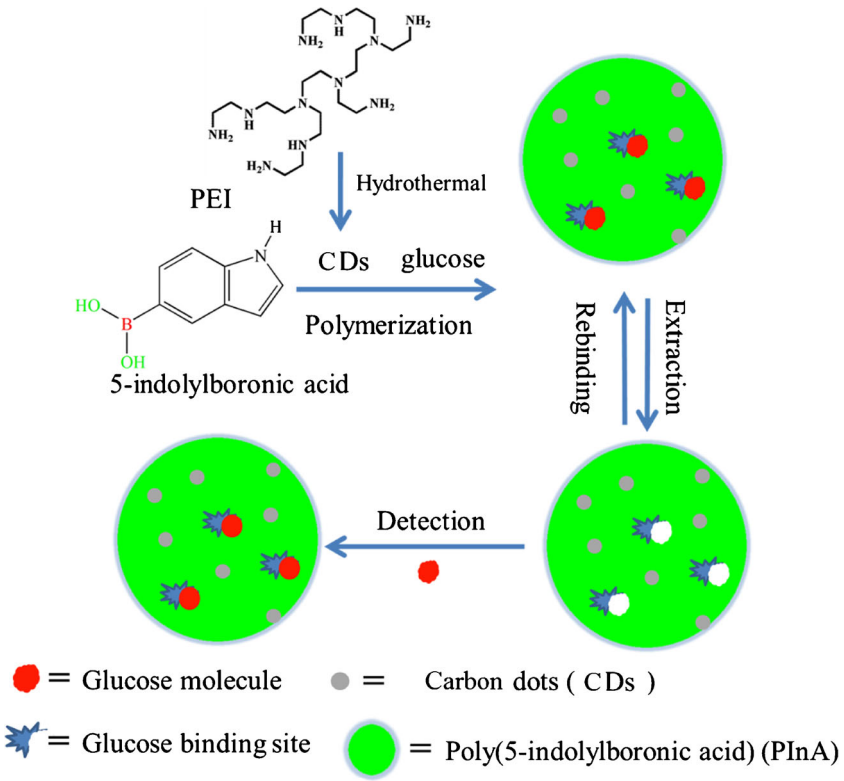
for glucose determination because they undergo cis-diol complexation with glucose. For fluorescent composites, they can serve as either fluorophores or quenchers. The tight but reversible recognition of diol-containing species gives rapid and sensitive response to glucose. [16, 21].

While boronic acid based optical materials have demonstrated high sensitivity for glucose detection, they are probably not suitable for practical glucose detection because they interact not only with glucose but with other saccharides as well [21, 22]. To enhance the selectivity of boronic acid based optical materials, MIPs are introduced as detection materials due to their selective response to the target molecule. However, there is a critical issue when using MIP in biological samples, the selective extraction and rebinding performance of MIP are sharply reduced when the materials fabricated in non-polar organic media are used in aqueous biological solvents. This is because the cavity induced by the template exfoliation probably generates deformation when MIP synthesized with non-polar solvents is applied in aqueous solutions. The superior selectivity and rebinding property of MIP can be retained when the samples are dissolved in the media used in the MIP preparation [18]. Herein, a boronic acid group-functionalized molecularly imprinted CDs hybrid was prepared as a novel PL probe for label free glucose detection (Scheme 1). The designed glucose-imprinted hybrid combines several key advantages into a single material, including simple preparation, tunable and stable fluorescent performance, outstanding structural stability and chemical inertness, and highly selective, sensitive, and reversible binding with glucose. Importantly, glucose can be well distinguished from both its analogues and the various potential interfering substances in a biological sample, which is beneficial for application as a practical platform for glucose monitoring.

Results and discussion

Choice of materials

Boronic acid groups are an ideal recognition element for the determination of saccharides, which have been studied widely [22]. Polyindole is an organic conductive polymer, which combines the optical and electronic performances of metals and semiconductors, showing many attractive properties such as corrosion inhibition property, thermal stability, and low toxicity. The polymer chains of polyindole, in combination with a boronic acid, lead to a novel polymer that is useful for the special recognition of glucose and other polyols by a change in its optical properties [20, 23]. Carbon dots have excellent PL properties with oxygen-containing functional groups, which serve the purpose of immobilizing the carbon dots around PInA.



Scheme 1 Preparation procedure of the glucose-imprinted CDs hybrid

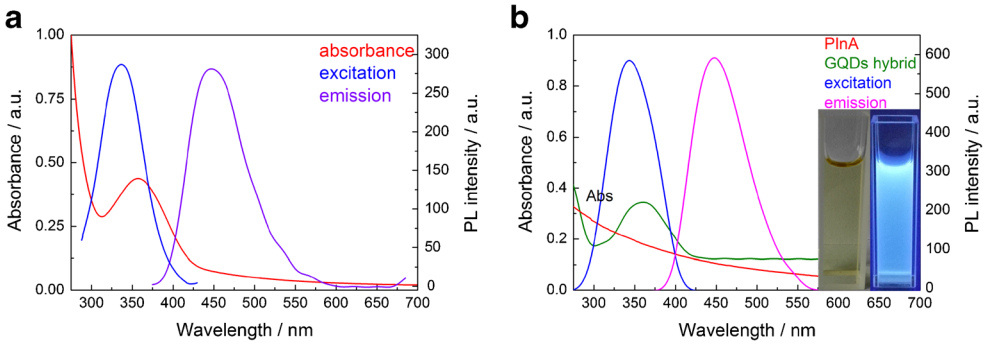


Fig. 1 **a** UV-vis absorption spectra of CDs (red), the excitation (blue) and emission (violet) fluorescence spectra of CDs. **b** UV-vis absorption spectra of PInA (red) and glucose-imprinted CDs hybrid (olive), the excitation (blue) and emission (magenta) fluorescence spectra of glucose-imprinted CDs hybrid, insets: Photographs of glucose-imprinted CDs hybrid taking under visible (left) and 365 nm UV lights (right)

Synthesis, composition, and morphology of CDs and the glucose-imprinted CDs hybrid

Our strategy for preparing the glucose-imprinted CDs hybrid involves the synthesis of the water-dispersible CDs bearing surface hydroxyl/carboxyl groups, followed by one-step fabrication of molecularly imprinted hybrid in the presence of boronic acid groups (Scheme 1). The optical performances of CDs and the glucose-imprinted CDs hybrid were assessed by UV-visible absorption spectra and fluorescence spectra. From Fig. 1a, an absorption peak of free CDs is observed at 353 nm, which may be ascribed to n-π^* transitions of the C = O bond and trapping of excited-stage energy by the surface states [24]. For the glucose-imprinted CD hybrid, there is a slight red shift for the absorption peak at 362 nm (Fig. 1b). This is because of the interaction between the aromatic rings of CDs and the poly(5-indolylboronic acid) (PInA) functional groups [25]. In contrast, pristine PInA has almost no absorption above 260 nm (Fig. 1b). In addition, the fluorescence spectra of both CDs (Fig. 1a) and the glucose-imprinted CDs hybrid (Fig. 1b) display a symmetric emission peak under the irradiation of exciting light. Moreover, a water-dispersed glucose-imprinted CDs hybrid solution displays an intense blue fluorescence color under UV light at 365 nm, showing a faint yellow color in sunlight (Insets in Fig. 1b). This fact suggests the free zig-zag effect with a carbine-like triplet ground state of $\sigma^1\pi^1$ and that the blue emission is originated from the intrinsic states in the highly crystalline structure [11].

The morphology of the prepared materials was characterized by TEM, and representative results are shown in Fig. 2. It is found that the CDs display a monodisperse nanoparticles structure distributed in the range of 3.5 to 9.3 nm with an average value of 7.1 nm (Fig. S1A). More details of individual CDs are presented in the HRTEM image (inset of Fig. 2a); the lattice fringe of 0.23 nm is in good agreement with that reported for 100 spaces of carbon [11]. The above results suggest that the CDs typically consist of dots based on carbon particles, which are arranged without apparent aggregation. Furthermore, the TEM image of the glucose-imprinted CDs hybrid (Fig. 2b) shows a typical microsphere structure with a part of the CDs at the periphery of PInA, which is probably due to the π–π interaction between the sp^2 π clouds of CDs and PInA [19]. Moreover, their size distribution ranges from 200 to 370 nm with an average diameter of 284 nm (Fig. S1B).

The surface and chemical composition were investigated using FT-IR spectrum and XPS. Figure 3a shows the FT-IR

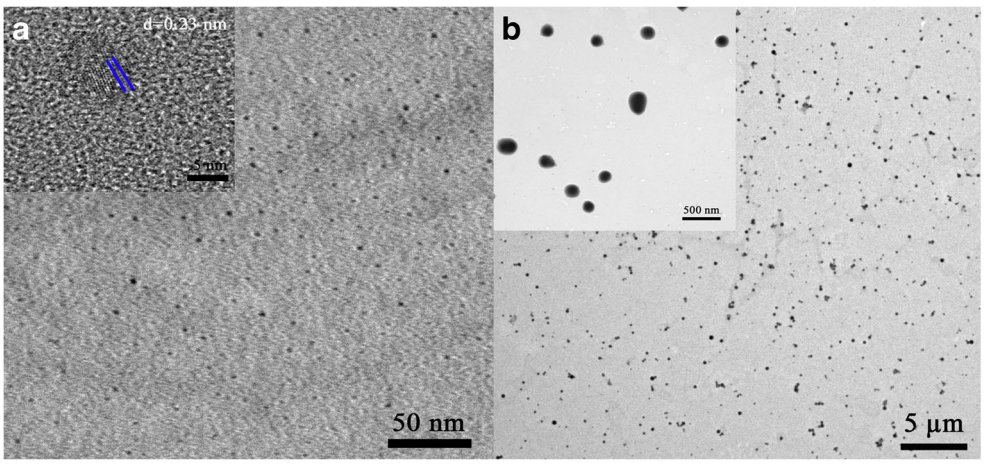


Fig. 2 **a** The TEM image of CDs (inset: the HRTEM image of CDs). **b** The TEM image of the glucose-imprinted CDs hybrid (inset: the enlarged TEM image of the glucose-imprinted CDs hybrid)

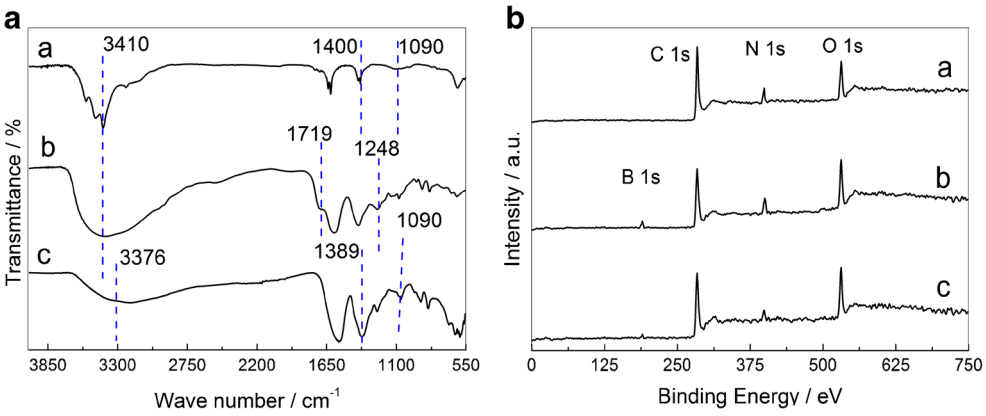


Fig. 3 **a** The FT-IR spectra of (a) PInA, (b) CDs, (c) the glucose-imprinted CDs hybrid. **b** The XPS spectra of (a) CDs, (b) PInA, (c) the glucose-imprinted CDs hybrid

spectra of PInA, CDs and the glucose-imprinted CDs hybrid. An obvious broad absorption peak at 3410 cm^{-1} suggests the presence of the stretching vibration bands of O − H. The vibrational absorption band of C − O and C = O conjugated with condensed aromatic carbons are observed at 1248 and 1719 cm^{-1}, respectively. These oxygen-containing functional groups not only help the CDs to be dispersed well in water but also form hydrogen bonds with PInA, thus immobilizing the CDs stably around the PInA. For the glucose-imprinted CDs hybrid, a new absorption peak of O − H groups at 3376 cm^{-1} appears due to the strong hydrogen bond between the surface carboxylic acid and hydroxyl groups of CDs and PInA. The C − N bonding vibration appears at 1389 cm^{-1} and is different from that of PInA at 1400 cm^{-1}, because of the protonation from the carboxylic acid groups of CDs [17, 26]. Additionally, the vibration absorption band at 1090 cm^{-1} that can be ascribed to B − O − H emerged in both PInA and the glucose-imprinted CDs hybrid, indicating the successful introduction of boronic acid groups [11]. For more insight, XPS measurements were performed. Figure 3b shows that the prepared glucose-imprinted CDs hybrid has four XPS peaks of C 1 s (284 eV), O 1 s (528 eV), N 1 s (400 eV), and B 1 s (190 eV) (Fig. S2), compared with those of CDs involving C 1 s (284 eV) and O 1 s (531 eV), and PInA involving C 1 s (284 eV), B 1 s (189 eV), N 1 s (400 eV), and O 1 s (529 eV) [21, 26]. This further confirms the existence of boronic acid groups.

Detection properties of the glucose-imprinted CDs hybrid

The resultant CDs and glucose-imprinted CDs hybrid demonstrates obvious responses at different pH values (Fig. S3). The fluorescence emission intensity of CDs is apparently pH-dependent, in which the fluorescence intensity reaches the maximum value in a neutral environment and is reduced in strong acidic and alkali solutions. This is attributed to the hydrogen bonds between the surface oxygen-containing groups of CDs in the acid condition, leading to aggregation and fluorescence weakening of CDs [21, 26]. On the other hand, the reducing fluorescence intensity in alkali solution is induced by the deprotonation of carboxyl groups in CDs, enhancing the electrostatic repulsions between them and overcoming the tendency of aggregation by layer-layer stacking. It is also observed that the fluorescence response of the glucose-imprinted CDs hybrid at different pH values shows a similar tendency to that of CDs. These results confirm the fact that the photoluminescence of CDs is derived in part from small sp^2 clusters incorporating with surface oxygen-containing groups including carboxylic groups, in which the chemical structure depends on the pH of the solution [27].

The fluorescence responses of the glucose-imprinted CDs hybrid and the non-imprinted CDs hybrid in the presence and absence of glucose were studied at different pH values. The fluorescence quenching efficiency (F_0/F, F_0 and F are the fluorescence intensities in the absence and presence of glucose, respectively) of the glucose-imprinted CDs hybrid at different pH values is superior to that of the non-imprinted CDs hybrid. Figure 4 demonstrates no obvious change in the fluorescence intensity.

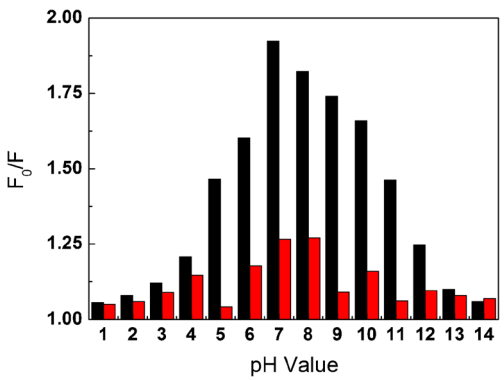


Fig. 4 Fluorescence responses of the glucose-imprinted CDs hybrid (black) and non-imprinted CDs hybrid (red) in the absence and presence of glucose at different pH values. F_0 and F are the fluorescence intensities in the absence and presence of 550 μM glucose, respectively

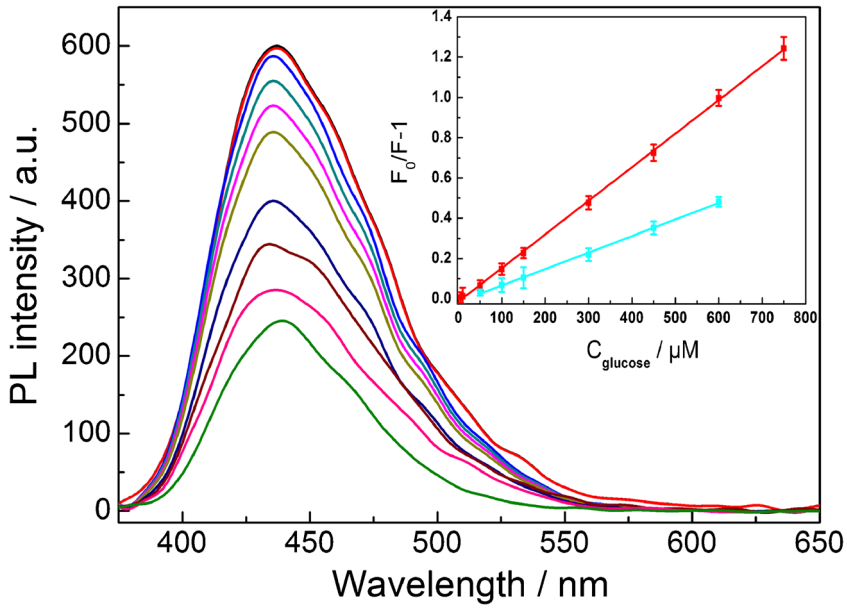


Fig. 5 Fluorescence responses of the glucose-imprinted CDs hybrid with addition of the indicated concentrations of glucose, which are 0, 5, 10, 50, 100, 150, 300, 450, 600, 750 μM (from top to bottom), respectively (inset: the calibration curve of glucose for the glucose-imprinted CDs hybrid (red) and the non-imprinted CDs hybrid (cyan) with addition of above mentioned concentrations)

These phenomena confirm the specific affinity of the molecularly imprinted CDs hybrid towards glucose. This is because of not only the binding sites but also the well-built imprinting cavities for glucose. Furthermore, we propose that the specific PL quenching of this glucose-imprinted CDs hybrid can be attributed to the formation of boronate complexes between glucose and the glucose-imprinted CDs hybrid. The boronic acid groups on the surface of the glucose-imprinted CDs hybrid allow covalent bridging of the two pairs of cis-diols of the glucose molecule, forming a large aggregation. With the formation of CDs assembly, the PL intensity becomes well-quenched [11]. A similar mechanism was reported in boronic acid functionalized inorganic quantum dots as the signal readout [28, 29].

Further research on the fluorescence quenching effect of glucose towards glucose-imprinted CDs hybrid solution at pH 7.0 is demonstrated in Fig. 5. It can be observed that the relationship between the fluorescence quenching efficiency and the concentrations of glucose can be satisfactorily fitted according to the Stern − Volmer equation:

$$F_0/F = 1 + K_{sv}/C_{glu}$$

where F_0 and F are the fluorescence intensities in the absence and presence of glucose, respectively. K_{sv} is the quenching constant of glucose, and C_{glu} is the concentration of glucose [19, 30–35].

When glucose is added into the system, it shows a good linear correlation between the concentration of glucose and F_0/F in the range of 5–750 μM with a correlation coefficient of $R^2 = 0.9913$. A limit of detection (LOD) of 0.5 μM is achieved for glucose determination based on the signal-to-noise ratio of 3. When a concentration of glucose higher than 5 μM is added into

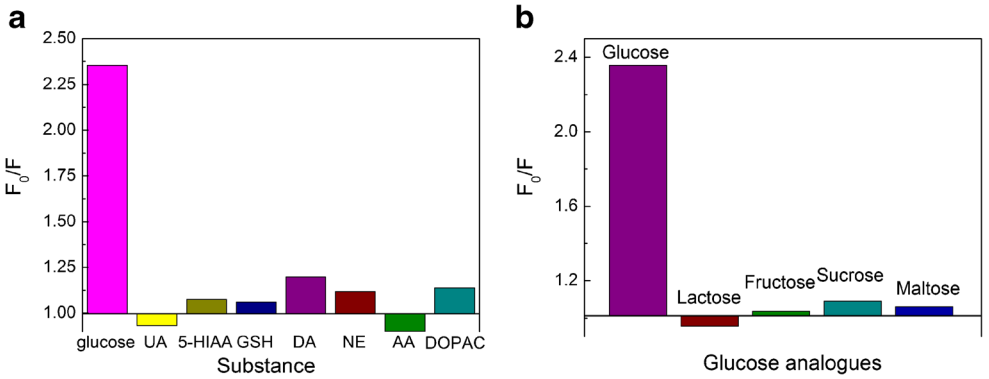


Fig. 6 **a** Fluorescence responses of the glucose-imprinted CDs hybrid towards a series of 800 μM potential interfering substances. **b** Fluorescence responses of the glucose-imprinted CDs hybrid in the presence of 800 μM different saccharides (glucose, Lactose, Fructose, Sucrose, Maltose). F_0 and F are the fluorescence intensities of the glucose-imprinted CDs hybrid before and after adding glucose and interferents, respectively

Table 1 Glucose assay in human serum

Sample[a]	Content (μM)	Added (μM)	Found (μM)	Recovery (%)	RSD (n = 3, %)
1	118	100	202	92.7	4.21
2	246	100	373	107.5	3.78
3	482	100	551	94.7	5.54

[a] The glucose concentrations in above samples are 118, 246 and 482 μM, respectively, which are in good agreement with the values measured by a commercial blood glucose monitor (109, 235 and 501 μM)

the system, due to the accessibility of the cis-diol units of glucose by the boronic acid group of the glucose-imprinted CDs hybrid, a large assembly containing CDs may form. With the formation of CDs aggregate, the fluorescence of CDs becomes well-quenched. The possibility of aggregate formation increases with increasing glucose concentration, with the PL intensity reducing linearly until the concentration of glucose is 750 μM. At a concentration of glucose more than 750 μM, the quenching tendency of the fluorescence of CDs slows down, because the excessive glucose cannot fully interact with the glucose-imprinted CDs hybrid. To our knowledge, the above results with a wider linear range and lower LOD are comparable to or better than those of previous quantum dots-based fluorescent detection systems (Table S1). To investigate the stability of the glucose-imprinted CDs hybrid, the fluorescent spectra were examined after the hybrid was stored for 10, 20, 30, and 45 days (Fig. S4). An apparent quenching is not discovered after 10 days. 95.4% of the fluorescent intensity is retained after 20 days, and 92.7% is retained after a month. After 45 days, 90.2% of the fluorescent intensity is still retained. The above results show that the prepared hybrid possesses excellent stability.

Effect of other biomolecules

To apply this analytical method to actual practice, a selectivity study was performed in the presence of possible coexisting interfering substances, including AA, DA, GSH, UA, NE, 5-HIAA and DOPAC. An obvious selective quenching effect by glucose is shown in Fig. 6a over other interferents in this assay. This result further confirms the outstanding specificity of the glucose-imprinted CDs hybrid towards glucose, which is mainly due to the specific binding between them as well as the tailor made imprinted cavities for glucose. Moreover, we also investigated the fluorescence behaviours of the prepared materials in the presence of the glucose analogues (maltose, lactose, fructose and sucrose). Figure 6b shows that the above four analogues have little effects (enhancement or quenching). Such high specific recognition is due to the stereostructure properties of glucose and the recognition mechanism of the present strategy. The boronic acid groups of the glucose-imprinted CDs hybrid are fastened by a pair of cis-diols in glucose forming large assemblies [16]. Unlike glucose, fructose has no additional cis conformational diol, which cannot cross-link the glucose-imprinted CDs hybrid and leads to the corresponding fluorescent quenching [21]. This is why no obvious change in PL is observed in the presence of fructose. Similar to the case for lactose, sucrose and maltose have no additional cis-diol units to change the PL of the glucose-imprinted CDs hybrid by cross-linking aggregation [25].

Detection of glucose in real samples

To demonstrate the potential applicability of the approach for glucose analysis, the detection of glucose in real samples was carried out. As shown in Table 1, the concentrations of glucose in human serum samples are in good agreement with the results measured by a commercial blood glucose monitor. Furthermore, standard addition experiments were also carried out. The recoveries of different known amounts of added glucose are obtained from 92.7 to 107.5%, and the relative standard deviation (RSD) is less than 5.54%. The outstanding recovery confirms excellent accuracy for glucose determination in biological samples, suggesting the practicability of the detection system.

Conclusion

In summary, we reported a boronic acid group functionalized molecularly imprinted CDs hybrid using glucose and indolylboronic acid. By taking advantages of CDs, molecular imprinting technique, and fluorescence spectroscopy methodology, the prepared glucose-imprinted CDs hybrid proved to be simple in design and economical in operation for glucose determination with high sensitivity and selectivity. More importantly, glucose detection in real human samples was achieved with satisfactory results, which may provide a new strategy for simple, low-cost and sensitive determination of glucose. However, because of the irreversibility of fluorescence response, this glucose-imprinted CDs hybrid is probably suitable for single-shot assays rather than online monitoring, which might be a challenge for fluorescence detection.

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Compliance with ethical standards The author(s) declare that they have no competing interests.

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